MICROBE ASSISTED GENERATION OF VALUE ADDED PRODUCTS FROM AGRICULTURAL WASTES

Synopsis of the work proposed for the Partial fulfilment of Ph.D. degree in Chemistry

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INTRODUCTION

World's population is increasing in leaps and bounds and with a robust increase in population, amount of waste generated is also increasing proportionately. In addition to this, amount of fuel consumed per person has also been increased and a hike in fuel prices has been noticed in last few years. The energy requirement in 2007 was reported to be 14 TW/y which is predicted to be about 28-30 TW/y in 2050 (Demirbas A. and Demirbas I. 2007). Waste generation and energy consumption have become problematic issue in society and there is an urgent need to solve these. Conventional energy sources which have been used since many decades are depleting rapidly hence we must switch over towards the alternative source (Demirbas A. and Demirbas I. 2007) of energy.

In the 20^{th} century, major researches have been done on the development of fossil crude oil, coal and natural gas to exploit the cheaply available fossil feedstock for development of industry to produce multiple products and energy to fulfil the growing demand of the present population (Bender M. et al 2000 and Bemirbas et al. 2006). Currently, 90% of energy resources are of fossil origin and their use is associated with the emission of CO_2 to the atmosphere. Our earth's atmosphere receives more than 15 billion tonnes of CO_2 every year. Global warming (Stern 2006) is the result of increased level of CO_2 in the atmosphere which is associated with the combustion of fossil fuels (Kamm B. et al. 2006). It is evident that accelerating global warming is the result of greenhouse gas emission. Carbon dioxide is considered as main greenhouse gas (IPCC 2001), but nitrous oxide, methane and several other components also contribute to greenhouse gases which cause more severe harm to global warming than CO_2 (Rutz D. et al. 2007).

USDA (United State Department of Agriculture) has defined value-added agricultural products as (Ernst & Tim Woods, 2011**)** "The Agricultural products can be said to be value-added if they fulfil one or all of the following criteria:

• A change in the physical state or form of the product.

• The production of a product in a manner that enhances its value, as demonstrated through a business plan.

•The physical segregation of a commodity or product in a manner that results in the enhancement of the value of that commodity"

Biofuels are the fuels which are produced through contemporary biological process such as, agriculture and anaerobic digestion, rather than fuels produced by geological processes such as formation of fossil fuels (coal and petroleum). Biofuels are the value-added products of agricultural residues. Biofuels can be characterised into three main groups; first, second and third generation biofuels which can be obtained from food, non-food feed-stocks and microalgae, respectively (Ragauskas et al. 2006) but more recently fourth generation biofuels are also introduced which are mainly solar fuels and electro-fuels (Eva-Mari Aro, 2016). Many food crops have been specifically grown for the production of bio-ethanol. However, bio-ethanol production from waste materials removed from fruits (pulp mill refuses and rinds) is not common (Itelima J. et al. 2013).

"First generation" biofuels are generally produced from agricultural crops (sugarcane, sugar beet, wheat, rice, soybean oil, sunflower and palm oil etc) and there is a highly mature technology in converting crops to biofuels (Jeihanipour and Bashiri, 2015). Although biofuel production is fruitful which can reduce CO_2 emission up to more than 80%, but on the other hand agriculture has to fulfil food necessities of 9 billion people, which is predicted growing world's population by 2050, and this is an enormous challenge from an agronomic perspective (Jeihampour A. 2011). The consideration of using crops for food or for biofuel may be referred to as "Food v/s Energy" conflict (Suurs and Hekkert 2009). Therefore, researchers have to decide to move on the production of second and third generation biofuels which can be obtained from non-food crops, grasses, agricultural and food wastes, algae etc.

The “second generation” biofuel production mainly focuses on the production of biofuels from the renewable resources, which could help to minimize the fossil fuel combustion and CO_2 emission in concern to prevent our “Earth” from global warming. Thus, the utilization of biomass resources is one of the most effective factors to protect our environment in 21st century (Chandra R. et al. 2012). The total annual global primary production of biomass is about 220 tonnes on dry weight basis that is equivalent to 4500 EJ of solar energy captured each year (Hall DO et al. 1998). The examples of wastes which can be used for second generation biofuel production are municipal solid wastes, used cooking oil, industrial wastes, agricultural wastes, and sewage sludge, which can produce biofuels such as biodiesel, bioethanol, bio-methanol, bio-butanol, biogas, bio-hydrogen (Jeihanipour and Bashiri, 2015).

The “third generation” biofuels are mainly derived from algae feedstock. Ethanol production in this era is not a big approach, but when using some renewable source, it may affect in fuel world. Bioethanol from algae feedstock are the biofuel which can also to be known as one of the most important renewable energy source (Chaudhary et al. 2014).

The “fourth generation” biofuels make use of novel synthetic biology tools and are just emerging at the basic research level. The fourth generation biofuels which are mainly photo biological solar fuels & electro-fuels and are expected to bring fundamental breakthroughs in the field of biofuels. Production of such solar biofuels is an emerging field technology and based on direct conversion of solar energy into fuel by use of raw materials that are inexhaustible, cheap and widely available (Eva-Mari Aro, 2016).

Agricultural biomass is a relatively broad category of biomass which includes the food based portions of crops (corn, sugarcane, beets, fruits) and non-food based portions (leaves, stalks, cobs of corn stover, orchard trimmings, rice straw, rice husk), perennial grasses, and animal wastes (Ralph EHS 2004). Fruit wastes (pulp mill refuse) are the part of cellulosic wastes (Pimentel et al. 2005). Globally cultivated top four major crops are wheat, maize, rice and sugarcane, respectively in terms of total cultivated area and production and produces majority of

lignocellulosic biomass in agriculture sector. Table 1 lists estimated world annual production of major agricultural crop based biomass (Chandra R. et al. 2012). All these four major crops yield about 5358.54 million tonnes of dry biomass. Though its major part is utilized as animal's feedstock but a huge part of this biomass is burnt in fields (Ralph EHS 2004).

Table 1: Estimated World Annual Production of Major agricultural crop based Biomass

Crop	**Total cultivated area (million hectare)**	**Total grain yield (million tonnes)**	**Average grain to aerial biomass ratio**	**Total estimated dry biomass (million tonnes)**
Maize	159.531	817.110	0.30 (Bolanos J. et al. 1993)	2723.70
Wheat	225.437	681.915	1.0 (Duke JA. 1983)	681.92
Rice	161.420	678.688	0.75 (Yoshida S. 1981)	904.92
Sugarcane	26.2	-	40 tonnes (Deren et al. 1991)	1048.00

In general, all types of biomass (McKendry 2002) which contain a large amount of carbohydrates, proteins, fats as main components can be used as substrates for biofuel production (Mital KM. 1996). It is predicted that lignocellulose based biomass can produce bioethanol (second generation biofuel) up to 442 billion L/year, though there is still no large scale plant for this purpose (Festel et al. 2014).

Wastes of interest: According to table 1 rice is the second major agricultural crop which provides about 905 million tonnes of dry biomass. Disposal of rice straw (RS) is problematic mainly because it is voluminous and light, more over because of its lignocellulosic content; it is not easily bio-degradable. It is disposed off mainly by combustion which is not environment friendly as it produces a large amount of carbon-dioxide. Energy can be extracted from rice straw via anaerobic digestion hence this biomass can be used for production of second generation biofuels (bio-ethanol and bio-methanol). This approach will be doubly beneficial for environment and will also help in reducing energy crisis.

Agra (The Taj city) is not famous only for Taj Mahal but it is also well known for its famous petha sweet which is prepared by petha fruit (*Benincasa hispida)* in the streets of Noori Darwaja. There are around 500 petha industries units running in Agra (Adesh Mohan 2001). These petha industries use coal for the processing of petha sweet. Supreme Court has banned the use of coal in Agra but most of these units are using it. Processing of petha to make it sweet involves treatment of petha fruit with lime water. After the treatment this used lime water discarded untreated. This petha waste water (PWW) discarded is highly alkaline and can be used for the pretreatment of rice straw. This petha waste water can be collected in the morning by taking appointment with the owner of petha industry. In addition to petha waste water, dairy waste water (DWW) is also discarded in a huge amount from dairy industry after preparation of dairy products. This DWW is acidic in nature and can also be used for pretreatment of rice straw. This can be collected from dairy industry in the morning time.

Hence it is proposed that rice straw would be the biomass used in the present research. Other wastes used along with rice straw will be Dairy waste water and Petha waste water.

Anaerobic digestion is the technique which can solve the two crucial problems of waste disposal and energy crisis at the same time. Energy can be extracted from wastes by its anaerobic digestion. This process leads to the production of methane, hydrogen and other forms of biofuels by degrading the organic waste which contains carbohydrate or sugar content in the presence of bacteria (Antoni et al. 2007). Hydrogen, methane, methanol, ethanol and butanol are renewable energy sources and have the capability to fulfil the energy demands and can also replace the conventional sources of energy. Biofuels formed during this anaerobic fermentation have remarkable applications in fulfilling the energy needs. In anaerobic degradation (Joyner A.E. et al. 1977 and Nandi R. 1998), anaerobic heterotrophic bacteria utilize organic feedstock in absence of light to produce biofuels [Rashika J. et al. 2010, Serpil et al. 2010, Ntaikou I. et al. 2010 and Guo Mei et al. 2010). Bio-methanol and bioethanol are the biofuels which can be extracted from this bacterial process and this includes the following steps:

- **Hydrolysis** (Parawira W. et al. 2005)**:** A reaction where particulates are solubilized and large polymers are converted into simple monomers.
- **Acidogenesis** (Garcia-Heras et al. 2003)**:** A biological reaction where simple monomers are converted into volatile fatty acids.
- **Acetogenesis** (De Bok et al. 2004)**:** Volatile fatty acids are converted into acetic acid, carbon dioxide, and hydrogen.
- **Methanogenesis** (Kalyuzhnyi, S. et al. 2000 and Hwang, S. et al. 2001)**:** Further, acetate and hydrogen are converted into methane and carbon dioxide, while hydrogen is consumed.

Main products of anaerobic digestion are:

- **Bio-hydrogen** (David B. et al. 2004)**:**

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$$

- **Methane or Consumption of hydrogen** (Thauer R.K. 1998)**:**

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Other biofuels like methanol and ethanol can be produced as:

Methanol production involves the biological oxidation of methane to methanol, based on methane mono-oxygenase activity of methanotrophic bacteria (Corder R.E. et al. 1986; Park and Lee, 2013). Methane produced during anaerobic digestion can be converted biologically into methanol by the following reaction:-

$$CH_4 + 1/2O_2 \rightarrow CH_3OH$$

Large scale production of methanol from natural gas and coal is a well-developed technology. Methanol prices today are competitive with hydrocarbon fuels. Methanol is a valuable liquid fuel and raw material for various synthetic hydrocarbon products. The petrochemical industries use methanol as raw material for production of various chemicals such as MTBE,

formaldehyde, acetic acid and biodiesel via trans-esterification (Khoshtinat M. et al. 2010). Methanol is a high octane liquid fuel which can be blended with gasoline and ethanol and can be used with today's vehicle technology at minimal incremental costs (Bromberg and Cheng, 2010). As fuel methanol is the most common type of alcohol's used for performing the esterification reaction, as it is the least expensive industrial alcohol. In comparison with ethanol, it has a lower price, higher reactivity, simpler recoverability, preventing soap property and azeotrope formation tendency (Siddiquee and Rohani, 2011).

Ethanol production (Saccharification and Fermentation) involves enzymatic production of ethanol in absence of oxygen using microbes such as *Saccharomyces cerevisiae* (Kothari et al. 2012 and Li C. et al. 2007).

$$C_6H_{12}O_6 + 2H_2O \rightarrow C_2H_5OH + CH_3COOH + 2CO_2$$

Bioethanol is currently the most common biofuel in terms of produced volume which is industrially produced mainly from corn and sugarcane (Jeihanipour and Bashiri, 2015). Production of ethanol from agricultural and biodegradable wastes provides a viable solution to multiple environmental problems simultaneously creating sink for waste and renewable energy production as well. Using ethanol-blended fuel for automobiles can significantly reduce petroleum use and greenhouse gas emissions (Wang et al. 1999). The production cost of ethanol from these agro-feed-stocks is more than twice the price of gasoline. The high feedstock cost poses a major obstacle to large scale implementation of ethanol as a transportation fuel (Reith et al. 2001). Bioethanol from these materials provides a highly cost effective option for CO_2 emission reduction in the transportation sector (Europe GM 2002).

LITERATURE CITED

Depletion of fossil fuels is of global concern. The demand for energy has been phenomenon due to the rapid development of certain growing economies, especially in developing countries. The problem of using fossil fuels can have an environmental impact due to the oxidation of CO_2, SO_2 and NO_2 emission. Also because of the environmental pollution from internal combustion engines, the increasing global concern has compelled the researchers worldwide to focus on the renewable alternative fuels (Mohan S. et al. 2014). In order to overcome these problems, there are alternative fuels that can replace fossil fuel such as hydrogen, bioethanol and other biofuels (Hossain et al. 2010). Fermentation processes using anaerobic microorganisms provide a promising path for converting biomass and agricultural wastes into chemicals and biofuels (Bahl et al. 1982). Acetone-butanol-ethanol fermentation (ABE fermentation) with the strict anaerobic bacterium, *Clostridium acetobutylicum*, is one of the most promising methods for biofuel production. Studies have been carried out to overcome the problem of energy crisis by using different types of biomass such as agricultural biomass, food wastes, fruit and vegetable wastes etc.

Ray et al. (2013) has explained in a review article on *Anaerobic Digestion* (AD) of Kitchen wastes and have identified AD an effective, controlled and enclosed version of anaerobic breakdown of organic wastes which releases methane. AD produces biogas which contains around 60 per cent of methane and 40 per cent of carbon dioxide (CO_2). The left over solid residue is called digestate which can be used as soil conditioner to fertilise land.

Methane generation potential of the major lignocellulosic agricultural crop biomass has been explored by Chandra R. et al. (2012). Furthermore, the methane production potential and its energetic analysis have also been compared with the bio-ethanol productions. The overall parametric analysis involved in anaerobic digestion and alcoholic fermentation explore that methane generation from lignocellulosic agricultural crop waste biomass is more economical and environmentally beneficial way of biomass utilization and also a sustainable way of energy production.

Biological production of methanol from methane using methanotrophs was proposed by Corder et al. 1986, applying ordinary temperature and pressure and found that high product yield in a single step reaction and simplified purification technology are possible with methanol as the only product. Methane consuming bacteria usually metabolize methane completely to CO_2, with methanol as an intracellular intermediate; therefore methanol production requires manipulation of the ordinary enzymatic reactions. A method of bio-methanol production from various kinds of biomass resources, such as sawdust and bark of Japanese cedar, chipped Japanese larch, bamboo, salix, cut waste wood from demolition sites, sorghum, and bran, straw, and husks was introduced by Nakagawa et al. (2005). Lignocellulosic resources (wood materials) and rice bran were also estimated to produce a high methanol yield (55% by weight), whereas rice straw and husks were estimated to produce lower methanol yield of 36% and 39%, respectively. In another study Park and Lee (2013) reported, the biological oxidation of methane to methanol, based on methane mono-oxygenase activity of methanotrophic bacteria. Oxidation is highly selective under mild condition, but conversion rate, yield and stability of catalytic activity should be improved for industrial methanol production. Since methanotrophic bacteria produces methanol as only precursor of formaldehyde which is further used to synthesize various essential metabolites. They have concluded that the direct use of bacteria for selective methanol production in a large amount seems unsuitable.

Ethanol production from hydrolysed agricultural wastes using mixed culture of *Zymomonas mobilis* and *Candida tropicalis* by acid, alkali and enzyme hydrolysis of fruit and vegetable residues has been reported by Patel and Lal (2007). Sharma et al. (2007) optimized the fermentation parameters for production of ethanol from kinnow waste and banana peels by simultaneous saccharification and fermentation using cellulase and co-culture of *Saccharomyces cerevisiae* G and *Pachysolen tannophilus MTCC 1077*. Periyasamy et al. (2009) also studied bioethanol production from sugar molasses using saccharification and fermentation. The optimal values of the parameters such as temperature, pH, substrate concentration, enzyme concentration and fermentation period were 35^0C, 4.0, 300 gm./L, 2 gm./L and 72 h respectively. Under these optimum operating conditions, 53% bio-ethanol yield was achieved.

Ethanol production from cotton-based waste textiles was studied by Azam Jeihanipour et al. (2009) using alkali hydrolysis to convert cotton and jeans into glucose followed by fermentation using *Saccharomyces cerevisiae* for conversion of glucose into ethanol. Production of ethanol, biogas, pectin and limonene from citrus wastes (CWs) through an integrated process was investigated by Pourbafrani et al. (2010). Hossain et al. (2010) produces bioethanol from rotten pineapples waste through fermentation by commercial yeast, *Saccharomyces cerevisiae.* The influencing parameters such as the effects of pH, temperatures, fermentation period, substrate concentration with and without water, components of pineapples from rotten and fresh ones were investigated. Alvarez et al. (2010) gave a methodology for optimising feed composition for anaerobic co-digestion using three wastes pig manure, tuna fish waste and biodiesel waste. Production of ethanol from mango (*Mangifera indica* L.) peel by *Saccharomyces cerevisiae CFTRI101* using the nutrient supplementation such as yeast extract, peptone etc. has been reported by Reddy et al. (2011). Hadeel et al. (2011) have also used *Saccharomyces cerevisiae* for the production of ethanol from rambutan fruit waste biomass.

Ding et al. (2011) investigated the potential of using coconut husk as substrate for bioethanol production. In this study, feasibility of using microwave-assisted-alkaline pretreated coconut husk as carbon source was investigated for batch ethanol fermentation using simultaneous saccharification and fermentation process. Simultaneously, coconut husk was treated with 20, 25 and 30% sodium hydroxide solution at 100 ^{0}C for 2-3 h under pressure to obtain the coconut husk cellulose for ethanol conversion by Vaithanomsat et al. (2011). For this process commercial enzymes celluclast 1.5L and Novozyme 188 were used for cellulose hydrolysis and yeast for ethanol fermentation. Delignification of coconut husk was also carried out by microwave assisted chemical pretreatment for biofuel production, using acids and bases. It was found that 3.5% microwave assisted NaOH shown best results in removing the lignin content and increasing the cellulose content, Laghari et al. (2015). The enzymatic production of bioethanol from cassava and sweet potato peels was examined using two groups of organisms, i.e. *Gloeophyllum sepiarium* and *Pleurotus ostreatus* to hydrolyse 20g, 35g and 50g of substrates at 28^{0}C for 7 days by Oyeleke et al. (2012). *Zymomonas mobilis* and *Saccharomyces*

cerevisiae were further used to ferment the substrates at 28^0C for 5 days. The fermented liquid was distilled at 78^0C and quantity of ethanol produced was determined. Vegetable and fruit wastes were converted into viable products using batch submerged fermentation by Kandari et al. (2012). The fermentable sugars in fruit peels were quite comparable for alcohol (14.6-15.2 w/v). The maximum alcohol was produced within 36 hours of fermentation in papaya peels extract followed by banana and apple peel extract (5.90-4.94%). In case of turnip peel extract the alcohol produced was 1.5 % (w/v). Almost 85-95% was observed in all four different set of experiment. The highest productivity was 0.83, 0.53 and 0.14g/l/h for papaya, apple and turnip peel extract respectively after 48h of incubation. Production of bioethanol from rice straw by popping pretreatment was studied by Wi, et al. (2013). The optimal doses of cellulase and xylase enzymes were 23 FPU and 62 IU/g biomass, respectively. Itelima et al. (2013) studied the production of bioethanol from banana peelings, plantain and pineapple peels by saccharification and fermentation process for 7 days, using co-culture of *Aspergillus niger* and *Saccharomyces cerevisiae*. Beside that, Bhandari et al. (2013) studied the production of biofuel from fruit rinds using *Tricoderma viride* and *Saccharomyces cerevisiae* for saccharification and fermentation respectively. The amount of ethanol produced after fermentation was analysed by gas chromatography and found to be highest for the same fruits with yields of $4.64g.L^{-1}$ and $4.38g.L^{-1}$ respectively. The results indicate the promising future for generation of ethanol from cellulosic wastes on a large scale. Bioethanol was also produced from corn and sweet potato used as substrate by solid submerged fermentation and saccharification with yeast for 72 hours, Meenakshi et al. (2014**)**. A cost effective method for production of ethanol from sugar beet and its estimation by modified dichromate method was introduced by Nakade Dhanraj B. (2014). In this method sugar beet roots were fermented by *Saccharomyces cerevisiae* at 30^0 C for 48 hours and estimation of produced ethanol was done with the help of modified dichromate method and found that this method is 99% effective for ethanol estimation. Production of bioethanol from Banana pseudo stem was investigated by Ingale et al. (2014) using different chemical and biological pretreatments. Two fungal strains *Aspergillus ellipticus* and *Aspergillus fumigatus were* reported for producing cellulolytic enzymes on sugarcane bagasse *which* were used under

co-culture fermentation on banana pseudo stem to degrade helocellulose and facilitate maximum release of reducing sugars. The hydrolysate thus obtained was fermented by *Saccharomyces cerevisiae NCIM 3570* to produce ethanol. Enzymatic hydrolysis of waste paper for bioethanol production was enhanced by using separate saccharification followed by fermentation, Guerfali et al. (2015) in which two types of waste papers i.e. news-papers and office papers were used. Hydrolysis step was conducted with a mixture of cellulolytic enzymes produced locally by *Trichoderma reesei Rut-C30* (cellulose over producing mutant) and *Aspergillus nigerF38* cultures. Surfactant pretreatment effect on waste paper enzymatic digestibility was studied and Triton X-100 at 0.5 % (w/w) has improved the digestibility of newspaper about 45 %.

Based on the above literature, the present research work would be focussed on the extraction of energy from agricultural wastes by saccharification of its lignocellulosic content.

OBJECTIVES

- Pretreatment of rice straw and bacterial culture separately for biofuel production.
- Effect of the above pretreatment methods on the optimal production of biofuels e.g. bio-methanol and bioethanol from mixed agricultural wastes would be studied.
- Isolation of appropriate bacteria responsible for biofuel production would be carried out.
- Correlation of results obtained would be studied using available statistical/mathematical tools.

METHODOLOGY

Reported pretreatment methods are either, physical, chemical or enzymatic. Attempt will be made to pretreat the lignocellulosic waste with another waste (acidic or alkaline in nature) instead of using chemicals. This pretreatment would enable the hydrolysis of the waste to simple sugars which can be fermented to biofuels.

- ✓ For enhanced production of biofuels from agricultural wastes, pretreatment of the rice straw and bacterial culture would be carried out separately.
- ✓ Biofuels produced would be quantified using Gas Chromatography.
- ✓ Initial and final (at the end of the process) surface analysis of the rice straw would be done by S.E.M.
- ✓ Isolation of bacteria responsible for respective biofuel production would be carried out (Corder R.E. et al. 1986).
- ✓ Optimization of the process will also be done so as to get better production yield.
- ✓ Statistical models will also be applied for the authentication of the results.
- ✓ In addition to this progress of the experiment will also be monitored using various physical parameters like glucose, chemical oxygen demand and total solid content.

REFERENCES

- Adesh Mohan, **2001**. "Petha (sweet) cluster Agra (Uttar Pradesh)". *Cluster development programme*, India.
- Álvarez J.A., Otero L., Lema J.M.**, 2010**. "A methodology for optimising feed composition for anaerobic co-digestion of agro-industrial wastes*". Bioresource Technology,* 101: 1153–1158.
- Bahl, H., Andersch W., Braun K., and Gottschalk G.**, 1982**. "Effect of pH and butyrate concentration on the production of acetone and butanol by Clostridium acetobutylicum grown in continuous culture". *European Journal of Applied Microbiology, Biotechnology*, 14: 17-20.
- Bender M., **2000. "**Potential conservation of biomass in the production of synthetic organics". *Journal of Resources Conservation & Recycling*, 30: 49–58.
- Bhandari Suhas V, Panchapakesan Arun, Shankar Naveen, Kumar H G Ashok, **2013. "**Production of Bioethanol From Fruit Rinds by Saccharification and Fermentation". *International Journal of Scientific Research Engineering & Technology (IJSRET)*, 2(6): 362-365.
- Bolanos J, Edmeades GO., **1993. "**Eight cycles of selection for drought tolerance in lowland tropical maize, I. response in grain yield, biomass, and radiation utilization". *Journal of Field Crops Research,* 31: 233–52.
- Bromberg L. and Cheng W.K., **2010. "**Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation". *PSFC/RR*-10-12.
- Chandra R., Takeuchi H., Hasegawa T., **2012**. "Methane production from lignocellulosic agricultural crop wastes: A review in context to second generation of biofuel production". *Renewable and Sustainable Energy Reviews*, 16: 1462–1476.
- Chaudhary Lalitesh, Pradhan Priya, Soni Nishant, Singh Pushpendra, Tiwari Archana, **2014. "**Algae as a Feedstock for Bioethanol Production: New Entrance in Biofuel World". *International Journal of ChemTech Research CODEN (USA)*, 6(2): 1381-1389.
- Corder R. E., Johnson E. R., Gaddy J. L., **1986**. "Biological production of methanol from methane, department of chemical engineering". University of Arkansas, 469-478.
- De Bok, F. A. M., Plugge, C. M., and Stams, A. J. M., **2004**. "Interspecies electron transfer in methanogenic propionate degrading consortia". *Water Research*, 38(6): 1368–1375.

- Demirbas A, Demirbas I., **2007.** "Importance of rural bioenergy for developing countries". *Energy Convers Manage*; 48: 2386–98.
- Demirbas MF, **2006.** "Current technologies for biomass conversion into chemicals and fuels". *Journal of Energy Sources,* A (2)8: 1181–8.
- Deren CW, Snyder GH, **1991. "**Biomass production and biochemical methane potential of seasonally flooded inter-generic and inter-specific saccharum hybrids". *Journal of Bioresource Technology*, 36: 179–84.
- Ding, Teck-Yuan, Hii, Siew-Ling, Ong, Lisa-Gaik-Ai, Ling, Tau-Chuan**, 2011**. "Investigating the potential of using coconut husk as substrate for bioethanol production". *International Conference on Biotechnology and Environment Management IPCBEE 18.*
- Dominik Antoni, Vladimir V. Zverlov, Wolfgang H. Schwarz, **2007. "**Biofuels from microbes: Mini Review". *Applied Microbiology Biotechnology*, 77: 23–35.
- Donghyun Park and Jeewon Lee, **2013. "**Biological conversion of methane to methanol". *Korean Journal of Chemical Engineering*, 30(5): 977-987.
- Duke JA., **1983. "**Handbook of energy crops". http://www.hort.purdue.edu/newcrop/duke energy/triticum aestivum.html.
- Ernst Matt & Woods Tim, **2011. "**Agriculture and Natural Resources, Family and Consumer Sciences". 4-H/Youth Development, Community and Economic Development, *http://www.ca.uky.edu/agecon/index.php*.
- Europe GM, **2002. "**GM Well-to-wheel analysis of energy use and greenhouse gas emission of advanced fuel/vehicle systems". *A European study*.
- Eva-Mari Aro, **2016**. "From first generation biofuels to advanced solar biofuels". *Springer*, 45: 24-31.
- Festel G, Würmseher M, Rammer C, Boles E, Bellof M, **2014. "**Modelling production cost scenarios for biofuels and fossil fuels in Europe". *Journal of Cleaner Production*, 66: 242-253.
- Garcia-Heras, J.L., **2003**. "Reactor sizing, process kinetics and modelling of anaerobic digestion of complex wastes". *Biomethanization of the organic fraction of municipal solid wastes*, *IWA, UK*, 21-58.

- Guerfali Mohamed, Saidi Adel, Gargouri Ali, & Belghith Hafedh, **2015.** "Enhanced Enzymatic Hydrolysis of Waste Paper for Ethanol Production Using Separates Saccharification and Fermentation". *Applied Biochemistry & Biotechnology*, 175: 25–42.
- Guo Mei, Trably Eric, Latrille Eric, Carrere Helene, Steyer Jean-Philippe, **2010**. "Hydrogen production from agricultural waste by dark fermentation: A review". *International journal of hydrogen energy*, 35: 10660-10673.
- Hadeel A., Hossain A. B. M. S., Latifa Khayyat, ALNaqeb Haitham, Abear Jama and Norah AlHewiti, **2011.** "Bioethanol fuel production from rambutan fruit biomass as reducing agent of global warming and greenhouse gases". *African Journal of Biotechnology*, 10(50): 10157-10165.
- Hall DO., Rosillo-Calle F., **1998. "**Biomass resources other than wood". *London: World Energy Council.*
- Hitoshi Nakagawa et al **2005**. "Bio-methanol Production and CO2 Emission Reduction from Forage Grasses, Trees, and Crop Residues". Presented at *the third USDA Symposium on Greenhouse Gases & Carbon Sequestration in Agriculture and Forestry, Baltimore, USA.*
- Hossain A. B. M. S. and Fazliny A. R.**, 2010**. "Creation of alternative energy by bio-ethanol production from pineapple waste and the usage of its properties for engine". *African Journal of Microbiology Research*, 4(9): 813-819.
- Hwang, S., Lee Y. and Yang, K., **2001. "**Maximization of acetic acid production in partial of swine wastewater". *Biotechnology and Bioengineering*, 75: 521-529.
- Ike A, Toda N, Tsuji N, Hirata K, Miyamoto K., **1997**. "Hydrogen photo production fromCO2-fixing microalgal biomass: Application of halotolerant photosynthetic bacteria" *Journal of Fermentation and Bioengineering*, 84(6): 606-609.
- Ingale Snehal, Joshi Sanket J., Gupte Akshaya, **2014.** "Production of bioethanol using agricultural waste: Banana pseudo stem*". Brazilian Journal of Microbiology* 45(3): 885-892.
- IPCC; Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Xiaosu D (eds), **2001**, Climate Change 2001: the scientific basis. "Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Chang (IPCC)". *Cambridge University Press, UK,* 944.

- Itelima J., Onwuliri F., Onwuliri E., Onyimba Isaac, and Oforji S.**, 2013**. "Bio-Ethanol Production from Banana, Plantain and Pineapple Peels by Simultaneous Saccharification and Fermentation Process". *International Journal of Environmental Science and Development,* 4(2).
- Jeihampour A, **2011**. "Waste textiles bioprocessing to ethanol and biogas". Chalmers University of technology, Götberg.
- Jeihanipour Azam and Bashiri Reihaneh**, 2015**. "Perspectives of Biofuels from Wastes". Chapter.
- Joyner AE, Winter WT, Godbout DM, **1977**. "Studies on Some Characteristics of Hydrogen Production by Cell-Free-Extracts of Rumen Anaerobic Bacteria". *Canadian Journal of Microbiology*, 23(3): 346-353.
- Kalyuzhnyi, S., Veeken, A. and Hamelers, B., **2000. "**Two-particle model of anaerobic solid-state fermentation". *Water Science Technology*, 41: 43-50.
- Kamm B, Gruber PR, Kamm M. **2006. "**Bio refinery industrial processes and products, status and future direction". 1–2. Weinheim: Wiley-Verlay Gmbtt and Co KGaA.
- Kandari Vikash and Gupta Sanjay, **2012. "**Bioconversion of Vegetable and Fruit Peel Wastes in viable product". *Journal of Microbiology and Biotechnology Research*, 2(2): 308-312.
- Khoshtinat M., Amin N.A.S. and Noshadi I., **2010. "**A Review of Methanol Production from Methane Oxidation via Non-Thermal Plasma Reactor". *World Academy of Science, Engineering & Technology*, 38: 354.
- Kothari R, Singh DP, Tyagi VV, Tyagi SK, **2012. "**Fermentative hydrogen production –an alternative clean energy source". *Renew Sustain Energy Rev*iew; 16: 2337–46.
- Krzysztof Biernat, Artur Malinowski and Malwina Gnat, **2013**. "The Possibility of Future Biofuels Production Using Waste Carbon Dioxide and Solar Energy". http://dx.doi.org/10.5772/53831.
- Levin David B., Pitt L., Love M., **2004**. "Bio-hydrogen production: prospects and limitations to practical application". *International Journal of Hydrogen Energy*, 29: 173-185.
- Li C, Fang HHP, **2007. "**Fermentative hydrogen production from wastewater and solid wastes by mixed cultures". *Critical Review Environmental Science Technology*; 37: 1–39.

- Meenakshi A., Kumaresan R.**, 2014**. "Ethanol Production from Corn, Potato Peel Waste and Its Process Development*". International Journal of ChemTech Research CODEN (USA)*, 6(5): 2843-2853.
- Melis A, Happe T., **2001**. "Hydrogen production. Green algae as a source of energy". *Plant Physiology*, 127(3): 740-748.
- Mital KM., **1996. "**Biogas systems: principles and applications". New Delhi, India*: New Age International (P) Limited.*
- Mohan Shashank, Jain Manish, Pal Amit, **2014**. "Indian Energy Crises and Biodiesel as Renewable Alternative Fuel". *International Journal of Emerging Technology and Advanced Engineering*, 4: 802.
- Mtui GYS., **2009.** "Recent advances in pretreatment of lignocellulosic wastes and production of value added products". *African Journal of Biotechnology*; 8(8): 1398- 1415.
- Nakade Dhanraj B**., 2014**. "Cost effective method for production of ethanol from sugar beet and its estimation by modified dichromate method". *Central European Journal of Experimental Biology*, 3(1): 9-12.
- Nandi R, Sengupta S., **1998**. "Microbial production of hydrogen: An overview". *Critical Reviews in Microbiology*, 24(1): 61-84.
- Ntaikou I., Antonopoulou G., Lyberatos G., **2010**. "Biohydrogen Production from Biomass and Wastes via Dark Fermentation: A Review". *Waste Biomass Valor*, 1: 21–39.
- Oyeleke, S.B., Dauda, B.E.N., Oyewole, O.A., Okoliegbe, I.N. and Ojebode, T. **2012**. "Production of Bioethanol from Cassava and Sweet Potato Peels". *Advances in Environmental Biology*, 6(1): 241-245.
- Ozmifci Serpil, *Kargi* Fikret, **2010**. "Comparison of different mixed cultures for biohydrogen production from ground wheat starch by combined dark and light fermentation". *Journal of Indian Microbial Biotechnology*, 37: 341–347.
- Parawira W., Murto M., Read J.S., Mattiasson B., **2005**. "Profile of hydrolases and biogasproduction during two-stage mesophilic anaerobic digestion of solid potato waste". *Process Biochemistry*, 40 (9): 2945-2952.

- Patel Sonali and Lal Banwari**, 2007**. "Ethanol production from hydrolysed agricultural wastes using mixed culture of Zymomonas mobilis and Candida tropicalis". *Biotechnology Lett*er, 29: 1839–1843.
- Perera Karnayakage Rashika J., Ketheesan Balachandran, Gadhamshetty Venkataramana, Nirmalakhandan Nagamany, **2010**. "Fermentative biohydrogen production: Evaluation of net energy gain". *International journal of hydrogen energy*, 35: 12224-12233.
- Peter McKendry, **2002**. "Energy production from biomass (part 2): conversion technologies". *Bioresource Technology* 83: 47–54.
- Pimentel D. and Patzek T. W., **2005.** "Ethanol Production Using Corn. Switch grass and wood; Biodiesel Production using Soybean and sunflower," *Natural Resources Research*, 14(1): 65-76.
- Pourbafrani Mohammad, Forgacs Gergely, Horvath Ilona Sarvari, Niklasson Claes, Taherzadeh Mohammad J., **2010. "**Production of biofuels, limonene and pectin from citrus wastes". *Bioresource Technology*, 101: 4246-4250.
- Ragauskas AJ **2006**, "The path forward for biofuels and biomaterials". *Science* 311(5760): 484-489.
- Ralph EHS., **2004. "**Biomass, bioenergy and biomaterials: future prospects. In: Anonymous, editor. Biomass and agriculture: sustainability, markets and policies". *OECD publication.*
- Ray N.H.S., Mohanty M.K., Mohanty R.C.**, 2013.** "Anaerobic Digestion of Kitchen Wastes: "Biogas Production and Pretreatment of Wastes, A Review", *International Journal of Scientific and Research Publications*, 3.
- Reddy Lebaka Veeranjaneya, Reddy Obulam Vijaya Sarathi and Wee Young-Jung, **2011. "**Production of ethanol from mango (*Mangifera indica* L.) peel by *Saccharomyces cerevisiae* CFTRI101'. *African Journal of Biotechnology*, 10(20): 4183-4189.
- Reith H et al **2001.** "Coproduction of bioethanol, electricity and heat from biomass wastes: potential and R&D issues". Paper *First European Conference on Agriculture & Renewable Energy, Amsterdam*.
- Rutz D, Janssen R., **2007. "**Biofuel technology handbook". Munchen, Germany: *WIP Renewable Energies.*

- Seung Gon Wi, In Seong Choi, Kyoung Hyoun Kim, Ho Myeong Kim and Hyeun-Jong Bae, **2013. "**Bio-ethanol production from rice straw by popping pretreatment". *Biotechnology for Biofuels*, 6: 166.
- Shanmugam Periyasamy, Sivakumar Venkatachalam, Sridhar Ramasamy, Venkatesan Srinivasan**, 2009**. "Production of Bio-ethanol from Sugar Molasses Using *Saccharomyces Cerevisiae". Modern applied science,* 3(8).
- Sharma Naresh, Kalra K. L., Oberoi Harinder Singh, Bansal Sunil, **2007**. "Optimization of fermentation parameters for production of ethanol from kinnow waste and banana peels by simultaneous saccharification and fermentation". *Indian Journal Microbial*, 47: 310–316.
- Siddiquee MN, Rohani S, **2011. "**Lipid extraction and biodiesel production from municipal sewage sludges: a review". *Renewable and Sustainable Energy Reviews* 15(2): 1067-1072.
- Stern N**, 2006**. "The economics of climate change: The Stern Review". Cabinet Office – HM Treasury. *Cambridge University Press*.
- Suurs RA, Hekkert MP, **2009, "**Competition between first and second generation technologies, lessons from the formation of a biofuels innovation system". *Energy*, 34(5): 669-679.
- Thauer R.K., **1998**. "Biochemistry of methanogenesis: a tribute to Marjory Stephenson". *Microbiology*, 144: 2377-2406.
- Vaithanomsat Pilanee, Apiwatanapiwat Waraporn, Chumchuent Nanthaya, Kongtud Wuttinunt and Sundhrarajun Sarima, **2011**. "The Potential of Coconut Husk Utilization for Bioethanol Production". *Kasetsart Journal of Natural Science*, 45: 159–164.
- Vaithanomsat Pilanee, Apiwatanapiwat Waraporn, Chumchuent Nanthaya, Kongtud Wuttinunt and Sundhrarajun Sarima, **2010**. "Possibility of Ethanol Production from Coconut husk Using Separate hydrolysis and Fermentation and Simultaneous Saccharification and Fermentation". *Proceedings of the 48th Kasetsart University Annual Conference, Kasetsart*, 3-5 March.
- Yoshida S., **1981.** "Fundamentals of rice crop science". Manila, Philippines: *The International Rice Research Institute.*